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PERMEATION OF OXYGEN BREATHING APPARATUS BY GASES AND VAPORS

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CONTENTS.

	Page.
Introduction.....	5
Former experiments on gases permeating rubber.....	6
Tests of oxygen breathing apparatus with gasoline.....	8
Tests with gasoline vapors.....	9
Test No. 1.....	9
Test No. 2.....	9
Test No. 3.....	10
Test with liquid gasoline.....	10
Test No. 4.....	10
Discussion of the results of tests.....	11
Tests of various fabrics for permeability.....	11
Description of apparatus.....	11
Results of tests.....	13
Special tests of fabrics containing glue-glycerine.....	21
Test for resistance to rough treatment.....	21
Test for resistance to weathering.....	21
Test in hot dry air.....	21
Test against cold.....	22
Summary and conclusions.....	22
Publications on mine gases and natural gas.....	23

TABLES.

TABLE 1. Results of distillation analyses of gasolines.....	9
2. Specifications of fabrics tested.....	14
3. Results of fabric tests with vapor of heavy gasoline.....	15
4. Results of fabric tests with vapor of very light casing-head gasoline.....	16
5. Results of fabric tests with benzene vapor, carbon monoxide, and natural gas.....	17
6. Computed permeation through breathing bags of different apparatus.....	20

ILLUSTRATIONS.

PLATE I. Original appearance of rubberized side of breathing-bag fabric.....	10
II. Rubberized fabric after immersion of breathing bag in gasoline.....	11
III. Apparatus for determining permeability of fabrics.....	12
IV. Curves showing permeability of fabric.....	18
FIGURE 1. Diagram of apparatus for testing permeability of fabrics.....	12
2. Permeation of gasoline and benzene vapors against pure rubber fabrics in two hours.....	18
3. Total volume of vapor permeating at 25° C., 1,000 square centimeters of fabric in two hours (liters).....	19

PERMEATION OF OXYGEN BREATHING APPARATUS BY GASES AND VAPORS.

By A. C. FIELDNER, S. H. KATZ, and S. P. KINNEY.

INTRODUCTION.

Question as to the permeability by gases and vapors of rubberized fabrics used in the breathing bags of self-contained oxygen breathing apparatus was raised recently by the death of James S. Cunningham, a foreman miner of the Bureau of Mines, who was overcome while wearing an oxygen breathing apparatus of the half-hour type in a large tank containing about 6 inches of gasoline at Trinidad, Colo. Investigation of the cause of his death indicated that the rubberized fabric of the bag had perhaps been penetrated by the vapor of gasoline. Experiments were therefore made with similar breathing bags in gasoline-saturated air. These experiments showed that when the gasoline used was highly volatile, like "casing-head" gasoline, dangerous amounts of it penetrated the bag. Several fabrics were then tested in a fabric-testing apparatus, such as is used by the Bureau of Standards for testing balloon fabrics, against gasoline and benzene vapors, carbon monoxide, and natural gas, in an attempt to find impermeable materials. The tests disclosed that rubber sheets one-sixteenth of an inch thick prevent penetration of the gases and vapors for at least two hours; this resistance is adequate for intermittent use followed by complete aeration, as the apparatus is designed for use during a two-hour period. Thinner rubberized fabrics were found impermeable when made by cementing two lightweight rubberized sheets together with a glue-glycerine layer between them; this fabric was supple, showed good resistance to deterioration from age, and completely prevented penetration of gases and vapors. A fabric impregnated and coated with a pyroxylin varnish proved flexible and quite resistant to the gases; it allowed a slight penetration of gasoline and benzene vapor, but not enough to be dangerous.

Though these tests showed that some fabrics now used for breathing bags were quite permeable to gasoline vapors in high concentrations, they did not show enough permeation in the relatively low

concentration produced by motor gasoline at ordinary temperatures to account for the death of Cunningham in the few minutes during which he was in the tank. The materials now in use on standard breathing apparatus are quite impermeable to the gases ordinarily encountered in mine-rescue work, but do not afford complete protection in high concentrations of gasoline and other organic vapors. For such purposes special impermeable fabrics seem desirable.

FORMER EXPERIMENTS ON GASES PERMEATING RUBBER.

Nearly a century ago, Dr. J. K. Mitchell, of Philadelphia, described his experiments¹ that demonstrated that rubber films are permeable to hydrogen sulphide, cyanogen, ammonia, carbon dioxide, nitrous oxide, arsine, olefiant gas, hydrogen, oxygen, carbon monoxide, and nitrogen. He roughly measured the rates of passage of these gases through a thin rubber film and determined the speeds to be in the above order, hydrogen sulphide being the fastest.

Soon afterwards Draper found that hydrogen sulphide at atmospheric pressure would pass through a rubber membrane into a hydrogen-oxygen-nitrogen mixture of 24½ atmospheres pressure, "as readily as if no such force were exerted against it."² Other gases acted similarly, and Draper concluded that a gas on one side of a permeable membrane acts as a vacuum toward another gas on the other side.

Thomas Graham observed that "gases penetrate most readily which are easily liquefied by pressure and which are also generally highly soluble in water or other liquids."³ Temperature has the following effects: It makes the gases less soluble, the rubber softer, and it increases the speed of diffusion; over a moderate range, 4 to 60° C., the combined effect of increasing temperature was to make the rubber film more permeable to air. Graham also tested rubberized silk and cotton cloth and found them much the same as the sheet rubber, both vulcanized and unvulcanized rubber were permeable. A few observations indicated the relation between thickness of rubber film and permeation to gas to be approximately in inverse ratio. The possibility of separating mixed gases by their differences in permeation through a membrane to vacuum was demonstrated. A gelatin film was tested for permeation, but without "marked results." He explained the process as a solution of gas in the rubber on one side, diffusion through to the other side, and evaporation there; a foreign gas on the evaporating side has no more effect than a vacuum.

¹ Mitchell, J. K., On the penetrativeness of fluids: *Am. Jour. Med. Sci.*, vol. 7, 1830, pp. 36-67. On the penetration of gases: *Ibid.*, vol. 13, 1833, pp. 100-112.

² Draper, J. W., On some mechanical functions of areolar tissues. Containing the coordination of the diffusion laws of Prof. Graham and the experiments of Dr. J. K. Mitchell: *Am. Jour. Med. Sci.*, vol. 22, 1838, pp. 23-44.

³ Graham, T., On the absorption and dialytic separation of gases by colloid septa: *Phil. Trans. Roy. Soc.*, vol. 156, pt. 2, 1866, pp. 399-439.

Studies of gases separated by soap and water films by Exner⁴ proved that the passage of each gas was proportional to its absorption coefficient or solubility in the liquid and inversely proportional to the square root of the density. Wroblewski⁵ demonstrated soon afterwards that the same relations hold for rubber films, and stated the relations with the formula:

$$Q = \Omega DS \frac{U_1 - U_2}{x} \cdot t$$

in which Q is the quantity of gas passed through a rubber of area Ω , and thickness x , in time t ; D is the diffusion coefficient of the gas; S the saturation coefficient of the rubber for the gas; and U_1 and U_2 measure the absorbed gas at the two surfaces of the rubber. His conclusions are in part as follows: Henry's law for gases and liquids apply for rubber and gases; the absorption coefficient for vulcanized rubber is a linear function of the temperature, for carbon dioxide and nitrous oxide it decreases with increased temperature, but for hydrogen it increases; the absorption is a purely physical phenomenon and not chemical; gases diffuse in rubber in accordance with the law that states the conductivity of solids for heat; this diffusion is independent of the chemical nature of the gas and is dependent only on the physical properties of the gas.

Experiments recently made by Rodt⁶ indicate that rubber completely free of moisture has only an exceedingly small permeability for carbon dioxide. This fact has no practical bearing on oxygen breathing apparatus, since rubber in contact with atmospheric air always contains moisture. Dewar⁷ has confirmed the effect of water by observing the change in rates of diffusion through rubber at the freezing point of water. He found that the effect of glycerin in checking diffusion was "very evident." In addition to some gases already mentioned, he demonstrated the permeability of rubber to vapors of ether, chloroform, benzene, alcohol, pyridine, and acetone-trile.

Recent work at the Bureau of Standards⁸ has confirmed many of the foregoing conclusions and in addition has shown that rubber

⁴ Exner, F., Ueber den Durchgang der Gase durch Flüssigkeitslamellen: *Ann. Phys. Chem.*, vol. 155, 1878, pp. 321-336, 443-464.

⁵ Wroblewski, S., Ueber die Diffusen der Gase durch absorbirende Substanzen: *Ann. Phys. Chem.*, vol. 158, 1876, pp. 539-568; Ueber die Natur der Absorption der Gase: *Ann. Phys. Chem.*, Neue Folge, vol. 8, 1879, pp. 29-52.

⁶ Rodt, V., Zur Fraze der Durchlassigkeit von Kantschuk fur Kohlensaure: *Chem. Zeit.*, vol. 38, 1914, pp. 1249-1251.

⁷ Dewar, J., Problems of hydrogen and the rare gases, * * * records of experiments: *Proc. Roy. Inst., Great Britain*, vol. 21, 1917, 543-560, and vol. 21, 1918, pp. 613-626.

⁸ Edwards, J. D., and Pickering, S. F., Permeability of rubber to gases: *Chem. and Met. Eng.*, vol. 23, July 7, 14, 1920, pp. 17 to 21, 71 to 75.

decreases in permeability with the degree of cure and with aging. The "impedance," or reciprocal of permeability of a given amount of rubber is greatly increased when the rubber is applied to cloth; in some cases it is nearly doubled. Most compounding materials are kept low when high impedance is wanted, though glue and paraffin are said to lower the permeability. The "specific permeability" was defined as the volume of gas permeating 1 square centimeter of rubber 1 centimeter thick with difference of partial pressure of 760 millimeters on the two sides in one minute; for hydrogen the specific permeability at 25° C. is 20.4×10^{-6} cubic centimeters per minute. Relative power of permeation of different gases were found to be as follows:

Power of permecation of different gases.

Nitrogen	0.16
Air	.22
Argon.....	.26
Oxygen.....	.45
Helium.....	.65
Hydrogen.....	1.00
Carbon dioxide.....	2.9
Ammonia.....	8.0
Methyl chloride	18.5
Water vapor (approximately).....	50.
Ethyl chloride	200.0

TESTS OF OXYGEN BREATHING APPARATUS WITH GASOLINE.

In order to determine the penetration of breathing bags by gasoline, tests were made with both the vapor and the liquid. The gasoline from Trinidad, Colo., that caused Cunningham's death, was a relatively nonvolatile motor gasoline. This gasoline and a very volatile casing-head gasoline were used in the tests. Table 1 gives the results of distillation analyses of the gasolines by Dr. E. W. Dean, of the Bureau of Mines petroleum laboratory. The analyses show the Trinidad gasoline to be typical of that generally sold throughout Colorado for motor fuel. The casing-head gasoline is much lighter and more volatile than any found in the motor-fuel market.

TABLE 1.—*Results of distillation analyses of gasolines.*

	Trinidad gasoline.	Casing-head gasoline.
Specific gravity at 15° C.....	0.765	0.6635
Degrees Baumé.....	53	81.5
Color.....	Yellow tinge.	Water white.
Odor.....	Good.	Good.
Acidity.....	None.	Positive.
Doctor test.....		Negative.
Unsaturation..... per cent..	4.5	3.0
	Barometer, 751 mm.; temperature, °C.—	Barometer, 743 mm.; temperature, °C.—
Amount distilled, per cent:		
First drop.....	60	33
5.....		37
10.....	96	40
20.....	111	45
30.....	123	49
40.....	135	54
45.....		57
50.....	147	59
60.....	160	64
70.....	172	71
80.....	185	80
90.....	207	97
95.....		125
Dry point.....	242	126
Distilled..... per cent..	97	96
Residue..... do....	1.2	0.5
Loss..... do....	1.8	3.5

TESTS WITH GASOLINE VAPORS.

The tests were made with a Salvus half-hour apparatus, the same as worn by Cunningham, and were arranged so that only the breathing bag was inside a tight box in which the space was kept saturated with the vapor. The main part of the apparatus was outside the box. Oxygen from the apparatus was breathed by a man in the usual manner. Gas samples were taken from the box at intervals to determine the concentration of gasoline vapor, also samples of the oxygen breathed were taken from a side tube in the mouthpiece.

TEST NO. 1.

Test No. 1 was made with the Trinidad gasoline in a room at 75° F. The concentration of gasoline vapor in the box at the beginning of the test was 4.3 per cent. The man breathing from the apparatus thought he detected gasoline in his oxygen in two minutes after the test started. Analysis of the inspired oxygen at that time showed 0.03 per cent gasoline vapor. The same man remained at the apparatus for 18½ minutes without suffering any ill effects. His place was then taken by another man who wore the apparatus until the oxygen was exhausted without noticing more than a trace of gasoline at any time. At the end of the test the inspired oxygen contained 0.07 per cent gasoline vapor. The total duration of the test was 38 minutes.

TEST NO. 2.

As it was thought probable that the temperature in the gasoline tank at Trinidad was higher than 75° F. and therefore caused greater

20311°—21—2

penetration, a second test was made several days later with another portion of the same gasoline but with a room temperature of 95° to 104° F. The wearer of the apparatus noticed gasoline in 12½ minutes after starting the test; at this time his inspired oxygen contained 0.7 per cent gasoline vapor. After detecting gasoline he continued wearing the apparatus for a period of 14½ minutes, when he became dizzy and stopped. At that time his inspired oxygen contained 0.28 per cent gasoline. Another man took his place and continued breathing for 14 minutes, when the oxygen became exhausted. Analysis of the oxygen at the end of the test showed 0.60 per cent gasoline and the man felt somewhat dizzy.

TEST NO. 3.

The next test was with casing-head gasoline in a room of about 78° F. Another oxygen apparatus of the same type was used. Analysis of the gas from the box showed 36 per cent gasoline vapor at the beginning of the test and 32 per cent at the end, 22 minutes later. Gasoline vapor was detected rather suddenly by the wearer of the apparatus in 9 minutes after beginning the test. A sample of oxygen from the mouthpiece then showed 1.13 per cent gasoline vapor. After breathing for three minutes more the man could endure the effects no longer. He had to hold to a table in order to stand and his sight became confused. Analysis now showed 2.22 per cent gasoline vapor in the oxygen. Three minutes later 2.60 per cent gasoline vapor was found in the oxygen. Another person attempted to breathe this mixture, but took only 10 or 12 breaths before he became quite dizzy.

TEST WITH LIQUID GASOLINE.

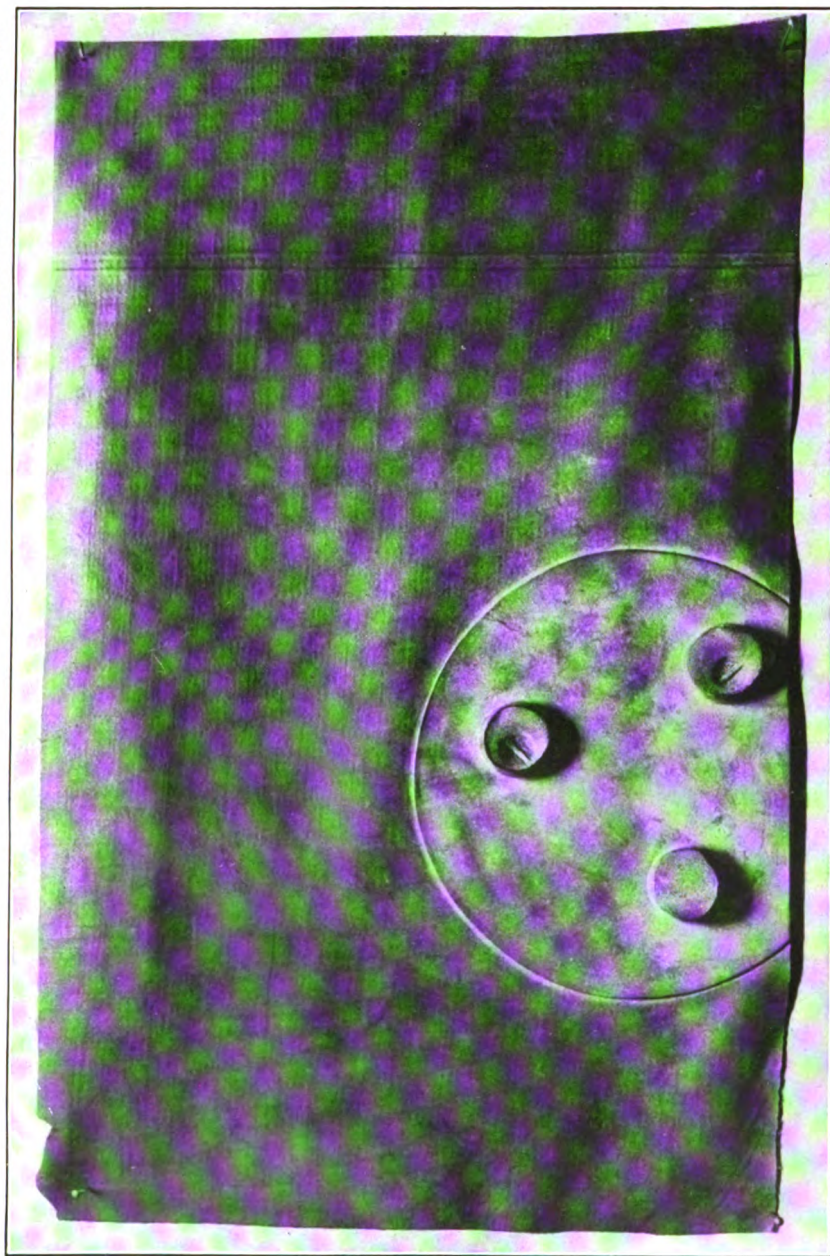
TEST NO. 4.

Test 4, with liquid gasoline, was performed with another similar apparatus, the breathing bag being partly submerged in ordinary motor gasoline having a gravity of 63° B. Half the bag was beneath the surface of the gasoline, and most of the bag was wet with the liquid. Four minutes after immersing the bag gasoline was noticed by the man breathing. Analysis showed 0.05 per cent gasoline vapor in the oxygen. The wearer continued breathing for 9 minutes more, when he thought the gas was becoming rather strong and felt he would soon be affected by it. The test was then stopped. The oxygen showed 1.09 per cent gasoline vapor. However, the wearer, a strong, robust man, did not feel any ill effects from the amount he inhaled during the experiment.

The total time of the immersion of the bag in gasoline was 13 minutes. Examination of the interior of the bag immediately after the test showed that the gasoline had penetrated and acted on the

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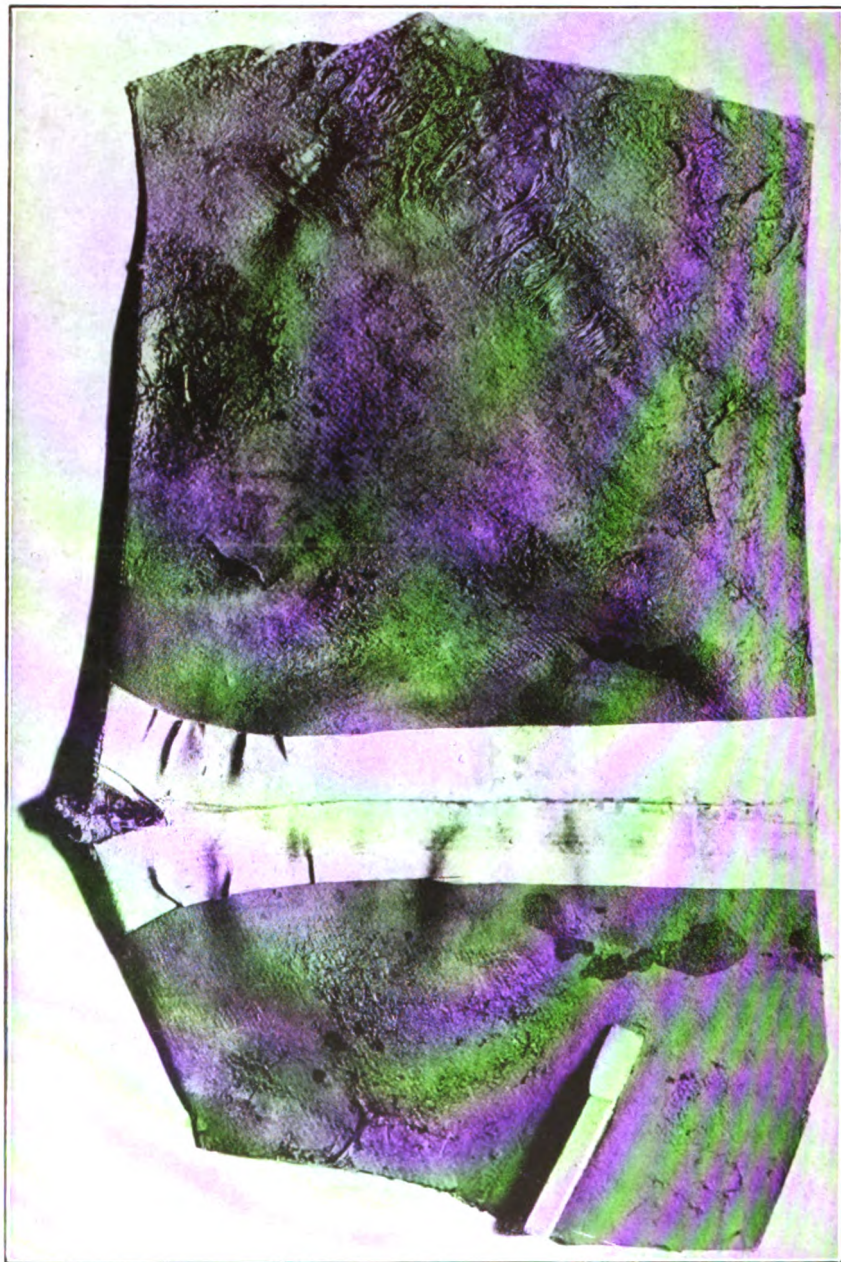
TECHNICAL PAPER 272 PLATE I



ORIGINAL APPEARANCE OF RUBBERIZED SIDE OF BREATHING-BAG FABRIC.

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TECHNICAL PAPER 272 PLATE II



RUBBERIZED FABRIC AFTER IMMERSION OF BREATHING BAG IN GASOLINE. SAMPLE TAKEN FROM BAG WORN BY CUNNINGHAM AT TIME OF HIS DEATH.

rubberized coating rendering it soft and sticky like rubber cement. The condition of the interior of the bag is pictured in Plate II. Plate I shows the appearance before immersion in gasoline. The action of vapors on the rubber produced no apparent change in its condition.

DISCUSSION OF THE RESULTS OF TESTS.

The experiments show that the thin rubberized coating on the apparatus tested is rather easily penetrated by both liquid gasoline and by such high concentrations of gasoline vapor as may be expected in a tank containing some volatile casing-head gasoline. Although ordinary motor gasoline does not seem to produce high enough concentrations of gas to penetrate, in dangerous quantities, in a period of 10 to 15 minutes a bag free from defects, yet the need of a much more impermeable bag is certainly demonstrated.

Actual tests of breathing bags of other apparatus have not been made, but all thinly-coated bags are permeable, as the later tests of fabrics show. Thus all oxygen breathing apparatus with such bags must be used with caution in high concentrations of gasoline or benzene and other organic vapors. A life line should always be attached to the wearer so that he can be immediately drawn out of the dangerous atmosphere should he show signs of distress.

TESTS OF VARIOUS FABRICS FOR PERMEABILITY.

Many types of oxygen breathing apparatus are not readily tested by the previous method, so subsequent experiments were made upon pieces of the fabrics. The testing apparatus was similar to the one devised by Edwards of the Bureau of Standards for testing balloon envelopes.⁹ Edwards has fully described this method and the principles involved, so only essential details will be briefly discussed here.

DESCRIPTION OF APPARATUS.

Figure 1 is a diagram of the apparatus; Plate III pictures it. The fabric to be tested was clamped in a circular "flange," or cell, so that it separated the space therein into two parts. Exactly 250 sq. cm. of fabric was exposed to the gas in the cell. Air mixed with the gas or vapor in question, of determined concentration, was circulated continuously at a rate at least $1\frac{1}{2}$ liters per minute through this system. A small blower of the Sirocco type, with a gas-tight stuffing box for the shaft, drove the air through tubes to a flowmeter, thence to a pressure regulator, to two gas-washing bottles in series, each containing 500 c. c. of gasoline (or benzene) and finally to the flange;

⁹ Edwards, J. D., Determination of the permeability of balloon fabrics; Tech. Paper 113, Bureau of Standards, 1918, 31 pp.

after passing through the flange the air returned to the blower. The flange, liquid gasoline, and most of the connecting tubing of the system were kept in a water thermostat at 25°C . The constant temperature and the large volume of gasoline, frequently renewed, automatically maintained uniform concentration of the vapor passing the fabric. Samples for determining concentrations were taken by inserting gas sampling bulbs with by-passes around them in the system between the saturators and flange; analyses were made with an

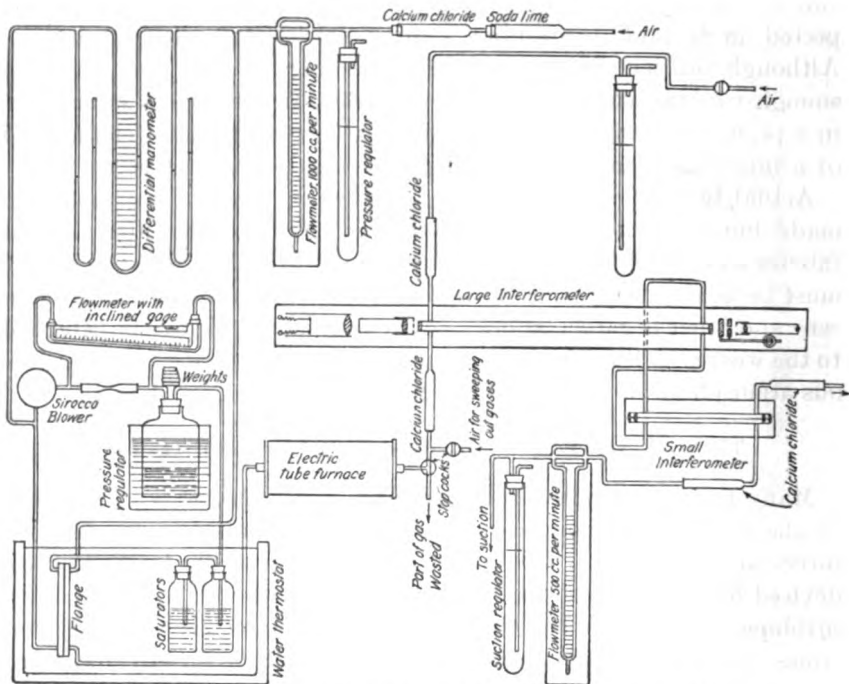


FIGURE 1.—Diagram of apparatus for testing permeability of fabrics.

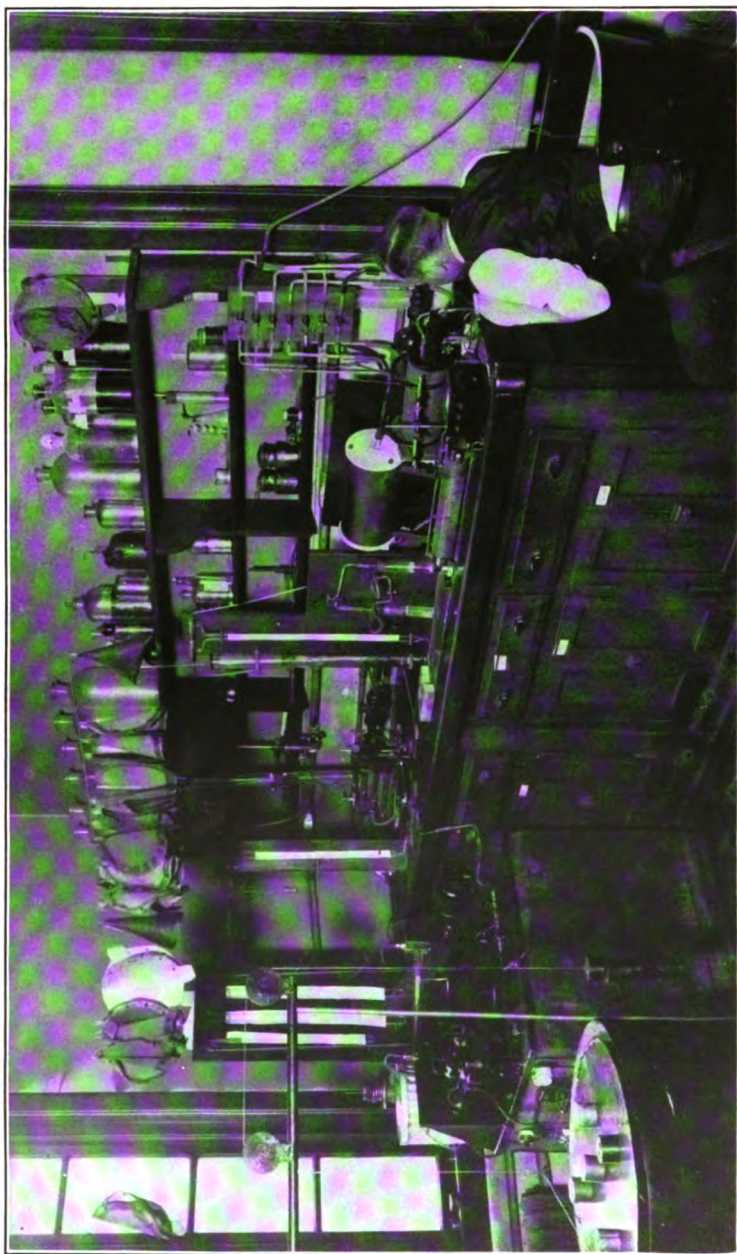
Orsat apparatus in a room temperature higher than 25°C . When gases instead of vapors were used for testing, a large gasometer containing the gas of predetermined concentration, was inserted in the system in place of the liquid saturators. The small loss of gas through the fabric made a negligible change in the concentration.

Pure air, free from carbon dioxide, was passed across the opposite surface of the fabric at a uniform rate of 1,000 c. c. per minute, measured by gas-flow meters of the resistance type.¹⁰ This air carried with it any gas which permeated. A part of the mixture escaped, 500 c. c. per minute were passed through two interferometers of the Rayleigh-Zeis type connected in series. These interferometers

¹⁰ Benton, A. F., Gas-flow meters for small rates of flow: Jour. Ind. Eng. Chem., vol. 11, 1919, pp. 623-629.

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TECHNICAL PAPER 272 PLATE III



APPARATUS FOR DETERMINING PERMEABILITY OF FABRICS.

were calibrated empirically against each gas or vapor by analyses of the original gases with the Orsat or Haldane method, and after they had been passed through a heated tube furnace following the interferometer. The results were expressed in terms of the volume of original combustible gas carried by a liter of air. The large interferometer had a high sensitivity but shorter range than the small one, the latter being used for the highest concentrations.

When tests were made with carbon monoxide, the gas passing from the flange to the interferometer was led through a heated tube furnace to form carbon dioxide, because the optical density of carbon monoxide so nearly equals that of air that the interferometer could hardly determine it. This procedure was not necessary for the other gases and vapors.

At the beginning of a test the apparatus was run for 10 minutes or more with the gasoline vapor passing through an auxiliary tube around the flange in order to saturate the circulating air. Adjustments were made so the pressure on the gasoline side of the system at the fabric was 3 cm. of water more than on the pure-air side, as indicated by the manometers. The interferometers were adjusted to indicate zero on the scales while the air only passed through. After everything was in readiness the vapor-air mixture was put through the flange, the time recorded and observations made at short recorded intervals with the large interferometer. Some time elapsed before the first gas permeated; when an immediate indication of gas and vapor showed passage of gas through pin holes, such tests were stopped and the fabric discarded. Two hours of testing a fabric completed an experiment.

RESULTS OF TESTS.

Table 2 gives the specifications of the different fabrics investigated. Tables 3, 4, and 5 give, respectively, the permeability of the fabrics by vapor of heavy gasoline, casing-head gasoline, and benzene; carbon monoxide showed no permeation when tested with these fabrics: Gibbs, 16 per cent concentration or carbon monoxide in air; rubber dam, 0.006 inch thick, 6 per cent concentration; leather, 30 per cent concentration. Natural gas from the mains at Pittsburgh, Pa., had approximately this composition.¹¹

¹¹ Burrell, G. A., Seibert, F. M., and Robertson, I. W., Analysis of natural gas and illuminating gas by fractional distillation at low temperatures and pressures: Bureau of Mines, Tech. Paper 104, 1915, 41 pp.

TABLE 2.—*Specifications of fabrics tested.*

Designation.	Description.	Thickness, total average inches.
Salvus.....	Twilled cotton cloth coated on one side with rubber about 0.012 inch thick. Used in breathing bag of Salvus half-hour apparatus.	0.022
Paul and Draeger..	Heavy duck, about 12 ounces per square yard, impregnated with rubber and one side coated with a rubber layer averaging about 0.015 inch thick, but decidedly variable because of uneven cloth surface. Used in breathing bags of both Paul and Draeger apparatus.	.045
Special Paul.....	Same as above except made with attempt to secure better impregnation of cloth.	.045
Gibbs.....	Loosely woven cotton twill, coated on one side with rubber averaging 0.020 inch thick.	.028
Fleus.....	Pure rubber of high quality, made without cloth, nominally $\frac{1}{8}$ inch thick.	0.063-.071
Rubber dam.....	Pure gum sheet rubber.....	.029
Do.....	do.....	.014
Do.....	do.....	.006
Gas bag.....	Material used for bags for holding gas for technical purposes, made of 2 fine cambric sheets cemented with a layer of rubber and covered on both outer surfaces with rubber.	.033
Balloon.....	3 sheets of fine light cloth cemented with rubber and rubberized on both outer surfaces. One side coated with aluminum powder.	.019
Glue-glycerin.....	1 piece of light cambric and 1 of light stockinette net, both rubberized thinly on one side, cloth sides cemented with thin layer of glue-glycerin mixture. Fabric quite flexible.	.023
Do.....	12-ounce duck and light cambric, coated with rubber on one side of each about 0.02 inch thick. Cloth cemented with glue-glycerin mixture.	.085
Pyroxylin.....	Close-woven cambric impregnated with pyroxylin varnish; coated on one side with layer of pyroxylin varnish 0.01 inch thick containing powdered aluminum.	.016
Leather.....	Sheepskin tanned and treated with mixture of rape, sperm, and neat's-foot oils.	.026
Fabricoid.....	Thin black muslin coated on one side with composition and surfaced to imitate leather. Contained pinholes.	.012
Do.....	Heavy twilled cotton cloth, one side composition coated to imitate black leather, used for upholstery; not supple.	.022

TABLE 3.—Results of fabric tests with vapor of heavy gasoline.

Gravity of gasoline, 53° B.
Source, Sinclair Refining Co., Trinidad, Colo.
Average formula of vapor penetrating fabric determined by Orsat combustion analysis, C_4H_{14} , or hexane.
Concentration of saturated vapor in air at 25° C. on one side of fabrics, 6.4 per cent by volume.

Test No.	Fabric, designation.	Thick- ness, total average (inches).	Time to first ob- served permea- tion (min- utes).	Volume of gas per minute per- meating 1,000 sq. cm. (c. c. at minute indicated).					Total volume of gas permeating from start through 1,000 sq. cm. (c. c. to minute indicated).					Remarks.
				Minute.					Minute.					
				15	30	45	60	75	15	30	45	60	75	
12 13	Salvus..... Average.....	0.022 6	{ 12 12	0.5 .4	4.2 4.2	8.9 8.0	10.8 10.8	10.8 10.8	0.5 .4	35.0 34.0	246 230	849 807	First permeation as determined by chemical test for carbon dioxide from burned gasoline showed in 6 minutes. In- terferometer first indicated at 12 minutes.	
14 15	Pauland Draeger. Average.....	.045 6	{ 6 6	.9 1.0	4.1 5.8	10.4 12.4	15.1 16.9	15.1 16.9	4.0 3.5	40 53	248 322	1,049 1,224		
37	Fleuss.....	.063	6	1.0	5.0	11.4	16.0	16.0	3.8	45.5	285	1,137		
21 22	Rubber dam..... Average.....	.029 78	{ 67 88				2.0 1.1	1.6				47 19	No permeation shown in two hours.	
9 16	Rubber dam..... Average.....	.014 24	{ 26 22		.1 .5	3.0 4.9	8.1 10.2	10.2		2 2.0	40 80	406 557		
19 23	Rubber dam..... Average.....	.006 3	{ 3 3	12.4 11.8	17.2 15.8	20.8 18.6	23.0 20.0	23.0 20.0	89.0 75.0	316.0 290.0	891 813	2,220 1,980		
17 18	Gas bag..... Average.....	.023 9	{ 8 10	.7 .6	4.5 4.2	9.6 9.1	11.9 12.4	11.9 12.4	2.5 2.0	39.0 33.0	259 244	929 914	No permeation. Do. Do.	
4 6 5	Glue-glycerin..... do.....	.023 6 .085	{											

TABLE 4.—Results of fabric tests with vapor of very light casing-head gasoline.

Gravity of gasoline, 81.5° B.
Average formula of vapor penetrating fabric determined by Orsat combustion analysis, C₄H₁₀, or pentane.
Concentration of saturated vapor in air at 25° C. on one side of fabrics, 30.1 per cent by volume.

Test No.	Fabric, designation.	Thick- ness, total average (inches).	Time to first ob- serva- tion (min- utes).	Volume of gas per minute per- meating 1,000 sq. cm. (c. c. at minute indicated).					Total volume of gas permeating from start through 1,000 sq. cm. (c. c. to minute indicated).					Remarks.
				Minute.					Minute.					
				15	30	60	120		15	30	60	120		
42	Salvus.....	0.022	4	79.0	102.0	113.0	116.0		450	1,850	5,100.0	12,000.0		
35	} Paul and Draeger.	.045	2	51.0	101.0	129.0	134.0		260	1,540	5,140.0	13,130.0		
45			3	76.0	122.0	151.0	174.0		460	2,010	6,210.0	16,210.0		
81	Average.....	.045	3	65.0	113.0	142.0	154.0		360	1,775	5,675.0	14,670.0		
82	Special Paul.....		1	65.0	91.0	117.0	125.0		500	1,720	4,960.0	12,350.0		
48	} Gibbs.....	.028	8	25.0	75.0	100.0	105.0		60	880	3,580.0	9,590.0		
82			9	28.0	89.0	114.0	120.0		80	1,080	4,200.0	11,350.0		
37	Average.....	.063	9	26.5	82.0	107.0	113.0		70	980	3,800.0	10,640.0		No permeation.
30	} Rubber dam.....	.029	22		4.0	69.0	76.0			10	1,200.0	4,450.0		
32			24		5.0	65.0	80.0			12	1,172.0	5,770.0		
44	} Average.....	.014	25		4.5	67.0	78.0			11	1,186.0	5,110.0		
47			1	133.0	200.0	218.0	220.0		708	3,340	9,670.0	22,810.0		
27	} Gas bag.....	.023	1	282.0	340.0	378.0	388.0		2,910	7,700	29,600.0	52,700.0		
38			5	66.0	96.0	106.0	106.0		327	1,610	4,680.0	11,040.0		
39	} Balloon.....	.019	5	34.0	72.0	80.0	101.0		105	980	3,450.0	9,220.0		
33			4	41.0	80.0	91.0	105.0		150	1,020	3,650.0	9,360.0		
79	Average.....	.022	5	38.0	76.0	90.0	103.0		128	1,000	3,550.0	9,290.0		No permeation. Same fabric as in test 33, but which had been exposed 30 days above boilers at temperature about 100° F.
80	do.....	.022												No permeation. Same fabric, but which had been folded in 4 directions at 1/4 inch intervals across entire surface and hammered on folds.
87	do.....	.022												No permeation. Same fabric, but which had been exposed to April-May weather for 29 days.
40	do.....	.085												
77	Pyroxilin.....	.016	52											
78	Leather.....	.026	1	211.0	267.0	296.0	307.0		1,210	4,950	13,480.0	31,790.0		

TABLE 5.—Results of fabric tests with vapor of benzene, carbon monoxide, and natural gas.

Concentration of saturated benzene vapor in air at 25° C., 12.8 per cent by volume.

Test No.	Fabric, designation.	Thickness, total average (inches).	Time to first oil-served permeation (minutes).	Volume of gas per minute permeating 1,000 sq. cm. (c. c. at minute indicated).				Total volume of gas permeating from start through 1,000 sq. cm. (c. c. to minute indicated).				Remarks.
				Minute.				Minute.				
				15	30	60	120	15	30	60	120	
57	Paul and Draeger.	0.045	7	8	26.00	41	50	25	283	1,330	4,100	No permeation.
58	Gibbs.	.028	8	6	27.00	39	43	18	290	1,320	3,830	
59	Heuss.	.023	30									
62	Rubber dam.	.029	3		04	23	75			300	3,420	Do.
61	do.	.014	5	21	48.00	59	60	84	518	2,180	5,760	
64	Balloon.	.019	6	11	24.00	33	35	492	1,380	3,420	8,160	
66	Blue-glycerin.	.022	14					38	329	1,220	3,250	
73	Pyroxylin.	.016	3	22	7.50	13	16		45	359	1,220	
74	Leather.	.026	3		34.00	37	42	147	581	1,650	4,050	

Composition of Pittsburgh natural gas.

Constituent.	Per cent.
Nitrogen	1.6
Methane	84.7
Ethane	9.4
Propane	3.0
Butane (chiefly)	1.3

This gas in 100 per cent concentration showed no permeation through Gibbs fabric, rubber dam 0.006 inch thick, pyroxylin, and leather.

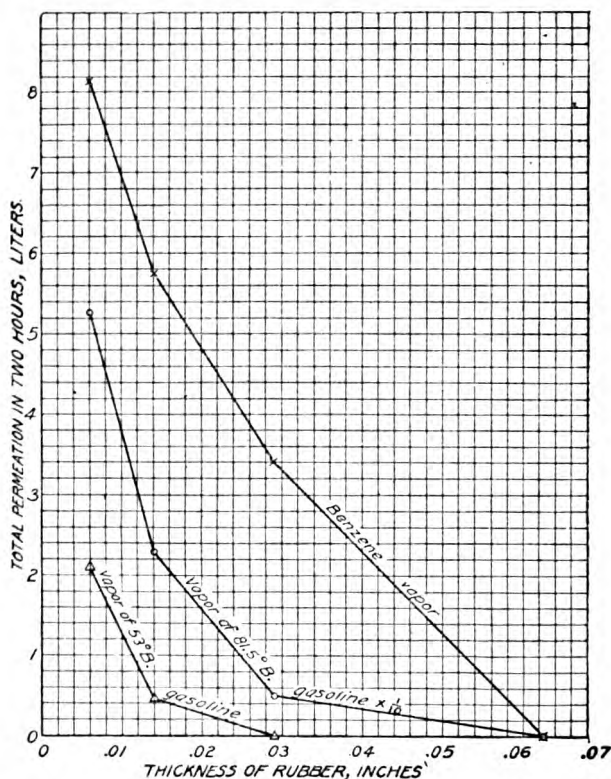
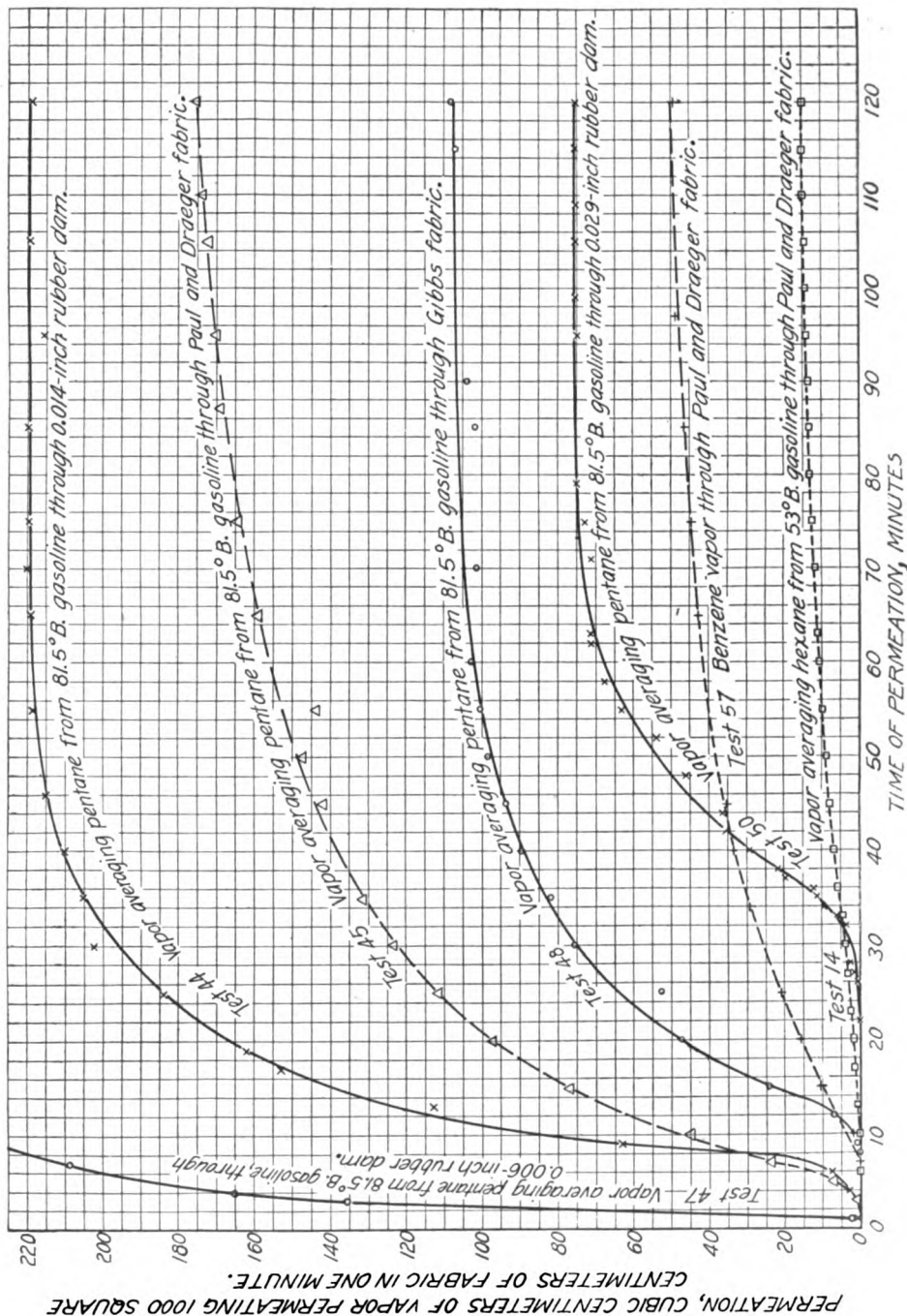


FIGURE 2.—Permeation of gasoline and benzene vapors against pure rubber fabrics in two hours.

Plate IV gives representative curves for some tests of permeation versus time. The graphs show that for a short time after the first penetration the quantity of gas coming through remains low, then there is a rapid increase which soon tends to attain a maximum.

Figure 2 shows the relations found for total permeation during two hours versus thickness of pure rubber fabrics. The curves are roughly hyperbolic, but no permeation was found during the two hours time through rubber one-sixteenth inch thick. These relations



accord with those of Edwards and Pickering,¹² who prove that permeability varies inversely as the thickness. They do not hold for fabrics containing cloth, because of different textures and differences in the impregnation.

Figure 3 shows graphically the total permeation for the vapors in two hours through the different permeable materials.

The fabrics used on the Salvus, Gibbs, Paul, and Draeger apparatus are all of cloth coated on one side with a thin layer of rubber, the latter two use the same fabric, which is impregnated as well as coated on one side with rubber. None of these fabrics proved impermeable.



FIGURE 3.—Total volume (liters) of vapor permeating, at 25° C., 1000 square centimeters of fabric in two hours.

The Salvus fabric gave a permeation against casing-head gasoline, as shown in Table 6, which would allow 9.9 per cent of vapor to accumulate in 15 minutes in the breathing apparatus, if there were no loss of vapor mechanically, by absorption in the lungs, or by outward permeation. In test 3 with the Salvus apparatus, which had conditions most like the flange tests, 2.60 per cent of vapor was found in the apparatus in 15 minutes exposure; considering the loss of vapor through the pressure release valve and actual loss by outward permeation and absorption in the lungs, the flange tests of fabrics give a satisfactory indication of what may be expected from apparatus in real service.

¹² Edwards, J. D., and Pickering S. F., Permeability of rubber to gases: Chem. and Met. Eng., vol. 23, July 7 and 14, 1920, pp. 17 to 21, 71 to 75.

The Fleuss bag material alone of those now in use proved completely impervious to all the gases during the two-hour period. The Fleuss has a bag of heavy, one-sixteenth inch thick, sheet rubber of pure, high quality and contains no cloth. Of course, if such a thick rubber bag were used repeatedly without intervening aeration the gasoline vapor would eventually penetrate into the bag.

TABLE 6.—*Computed permeation through breathing bags of different apparatus.*

Temperature, 25° C.

Figures have been calculated from fabric tests on the assumption that accumulated vapors have no tendency to permeate outward and that all are retained in the breathing apparatus.

Apparatus.	Area of bag.		Volume In bag and appa- ratus, approx- imate, liters.	Vapor.		Time to first permea- tion, minutes.	Concentration of vapor in apparatus, percent- age at minute indi- cated.			
	Square centi- meters.	Square inches.		Description.	Concen- tration around bag, per cent by volume.		Minute.			
							15	30	60	120
Salvus.....	2,207	342	10	Gasoline, 53° B. liquid.....	6.4	12	0.01	0.76	5.3	18.3
				Gasoline, 81.5° B. liquid.....	30.1	4	9.9	41	113	265
				Gasoline, 53° B. liquid.....	6.4	6	.08	.95	5.8	23
Paul.....	3,071	476	15	Gasoline, 81.5° B. liquid.....	30.1	3	7.4	36	116	300
				Benzene.....	12.8	7	.5	5.8	27	84
				Carbon monoxide.....	11		(1)	(1)	(1)	(1)
				Gasoline, 53° B. liquid.....	6.4	6	.1	1.4	8.4	34
Draeger....	4,433	687	15	Gasoline, 81.5° B. liquid.....	30.1	3	11	53	169	433
				Benzene.....	12.8	7	.7	8.4	39	121
				Carbon monoxide.....	11		(1)	(1)	(1)	(1)
Gibbs.....	2,262	351	11	Gasoline, 81.5° B. liquid.....	30.1	9	1.4	20	80	219
				Benzene.....	12.8	8	.4	6	27	79
				Natural gas.....	100		(1)	(1)	(1)	(1)
				Gasoline, 53° B. liquid.....	6.4		(1)	(1)	(1)	(1)
Fleuss.....	2,890	448	15	Gasoline, 81.5° B. liquid.....	30.1		(1)	(1)	(1)	(1)
				Benzene.....	12.8		(1)	(1)	(1)	(1)

¹ No permeation.

All the rubberized fabrics made with the glue and glycerin were completely impermeable even with a total thickness of only 0.022 inch (1/64 inch=.0156), about one-third of that needed for pure rubber. They were also supple and had properties seemingly useful for bags. In order to test them more severely for qualities other than permeability, special tests, described later, were arranged.

Fabrics specially made for laboratory gas bags and balloon envelopes containing two and three layers of strong, light cloth with rubber between and on the outer surfaces were also tested. They were permeable, much the same as breathing bag fabrics now in use.

Fabracoid in the thin quality was found to contain pin holes. The heavier quality was stiff and did not seem resistant enough to rough mechanical treatment; no permeation tests were made with it. Leather, oil treated, of the kind used in the diaphragms of dry gas meters,¹³ was highly permeable to gasoline and benzene vapors.

¹³ Lamb, M. C., The deterioration of leather used in gas meters: Jour. Soc. Chem. Ind., vol. 35, 1916, pp. 989-993.

Cloth impregnated and coated with pyroxylin varnish was found impermeable during the two-hour tests against carbon monoxide and natural gas. Small quantities of benzene and gasoline came through toward the close of the tests, but not enough to be dangerous. A little increase in the thickness of the coating would entirely prevent passage. This fabric offers possibilities as a substitute for rubber, as it may not deteriorate with age as rapidly as the rubberized fabrics.

No permeation of carbon monoxide or natural gas was found through rubber dam, 0.006 inch thick, rubberized fabrics, or leather during the two-hour testing periods.

SPECIAL TESTS OF FABRICS CONTAINING GLUE-GLYCERINE.

Special tests were made to determine the ability of fabrics containing glue-glycerin mixtures to withstand rough mechanical treatment, extremes of heat and cold, dry air, and weathering. The fabric selected for the tests was 0.022 inch thickness; it was made for gas-mask purposes and was nearly two years old at the time of the tests. It passed all tests in a satisfactory manner.

TEST FOR RESISTANCE TO ROUGH TREATMENT.

A piece of the fabric cut for insertion in the flange was folded and creased in parallel lines one-half inch apart over its entire surface; each fold was laid on a smooth board and hammered along its whole length with a 21-pound weight held in the hand and raised 4 to 6 inches; the process was then repeated on folds at right angles, then on the two diagonal directions, making four directions of folds. Though the surface was abraded in some places, the fabric did not show displacement of rubber or glue-glycerin mixture, nor did it develop any cracks. On testing for permeation against casing-head gasoline, negative results were found through two hours.

TEST FOR RESISTANCE TO WEATHERING.

A piece of the fabric was tacked to a board and placed on the south roof of a building, the roof having a slope of about 45°, where it was exposed to sun and weather from April 7 to May 5. At the end of the 29 days the exposed surface showed a slight checking, the under surface showed no change, the fabric retained its original flexibility, and the glue-glycerin held even at the edges. Tested against casing-head gasoline, it showed no permeability.

TEST IN HOT DRY AIR.

A piece of the fabric was hung for one month above boilers in continuous operation in a power house. Observations of temperature showed a maximum of 108° F. and minimum of 95°. Relative hu-

midity ranged from 63 to 25 per cent. At the end of the test the fabric retained its original flexibility and appearance and showed no permeability to casing-head gasoline.

TEST AGAINST COLD.

A test piece was laid on ice in an ice box over night. It retained its flexibility entirely.

SUMMARY AND CONCLUSIONS.

Tests were made to determine the permeability of the rubber bags of oxygen apparatus to gases and vapors. The breathing bags in vapor of volatile casing-head gasoline showed dangerous penetration; in one test 2.60 per cent of gasoline vapor was in a breathing bag after 15 minutes exposure to air containing about 34 per cent of casing-head gasoline vapor.

Further measurements of permeability were made of separate pieces of fabrics in a special apparatus. Tests lasted two hours, which is the time the larger oxygen breathing apparatus are designed to be worn. All the fabrics now used by the Bureau of Mines for breathing bags, excepting the Fleuss, proved permeable to gasoline and benzene vapors, and undoubtedly to other similar organic vapors. No permeation of the fabric investigated was found for carbon monoxide or natural gas. The impermeable (in two hours) Fleuss material consisted of heavy sheet rubber, one-sixteenth inch thick, made of high quality stock; no cloth was used in it.

Fabrics made of two rubberized sheets cemented with a glue and glycerin mixture were found completely impermeable; one such fabric had a total thickness one-third that required for rubber. Special tests for resistance to rough mechanical treatment, exposure to weather, hot dry air, and freezing temperature were passed by this fabric without permeation or loss of flexibility. A fabric made of cloth impregnated and coated on one side with pyroxylin varnish allowed only a slight penetration of gasoline and benzene vapors toward the close of the two-hour test period, not enough to be dangerous. A slightly thicker coating would entirely prevent penetration. This fabric has apparently very desirable properties for use in breathing bags, and deteriorates less than rubber with age.

Final recommendations regarding the use of heavy rubber, glue-glycerin, or pyroxylin fabrics in the breathing bags of different apparatus will depend upon the results obtained in actual use of these fabrics during the coming year in oxygen breathing apparatus used by the Bureau of Mines.

In the meantime due caution should be observed whenever oxygen breathing apparatus is worn in organic vapors. A life line should be attached to the person, so that on signs of distress he may be immediately withdrawn from the dangerous atmosphere.

PUBLICATIONS ON MINE GASES AND NATURAL GAS.

A limited supply of the following publications of the Bureau of Mines has been printed and is available for free distribution until the edition is exhausted. Requests for all publications can not be granted, and to insure equitable distribution applicants are requested to limit their selection to publications that may be of especial interest to them. Requests for publications should be addressed to the Director, Bureau of Mines.

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PUBLICATIONS AVAILABLE FOR FREE DISTRIBUTION.

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